B5

Rational design with input from DFT calculations and preparation of coordination polymer-based quantum magnets

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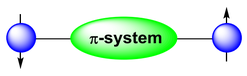
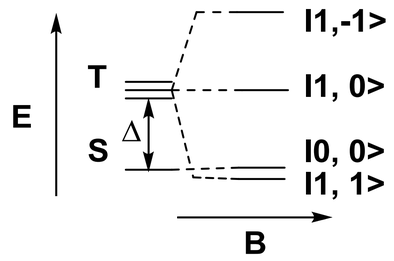
Introduction

There is a continuing challenge to develop magnetic materials from organic matter.[1] The choice of the nitronyl nitroxide radicals has been dictated by their stability, versatility and ability to self-organize. For magnetic field-induced Bose-Einstein condensation phenomena in solid state [2] weakly antiferromagnetically coupled diradicals were synthesized (J /k_B~ -10 K) with singlet ground state which can be switched by magnetic field into the triplet state. These biradicals can serve as molecular models of a gas of magnetic excitations.

Spin-dimer system
- total spin S=1;
- ground state: singlet.





$\Delta = J_{intra}$, $B_{c1} \approx 10$ T <=> $J_{intra}/k_B \approx 7$ cm^{-1}

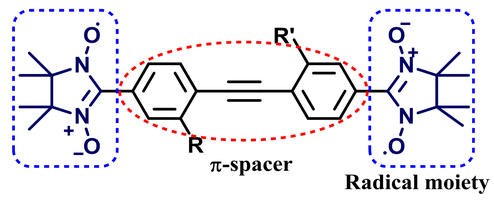
Spin Hamiltonian: H = -2*J*S1*S2

Broken symmetry (BS) approach:

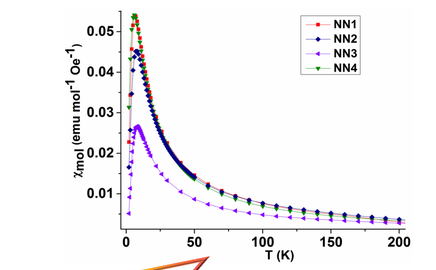
$$J_{intra} = (E(BS) - (E(T)) / (S^2(T) - S^2(BS)) \sim E(BS) - E(T)$$

[1] C Train, L Norel, M Baumgarten, *Coord. Chem. Rev.*, **253**, 2342 (2009)
[2] T. Gimarchy, C. Rüegg, O. Tchernyshyov *Nat. Phys.* **4**, 198 (2008).

Tolane Derivatives

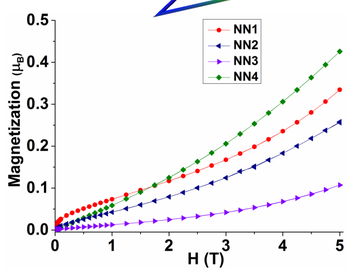


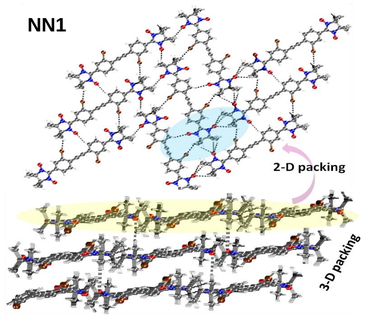
NN: R,R'= H
NN1: R,R'= Br
NN2: R= H, R'= $CONH_2$
NN3: R= Br, R'= OMe
NN4: R= H, R'= NO_2

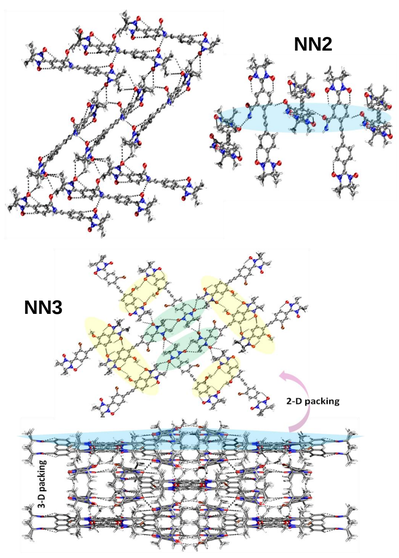


Intra-molecular magnetic exchange interactions are preserved

Fine tuning of inter-molecular magnetic exchange interactions





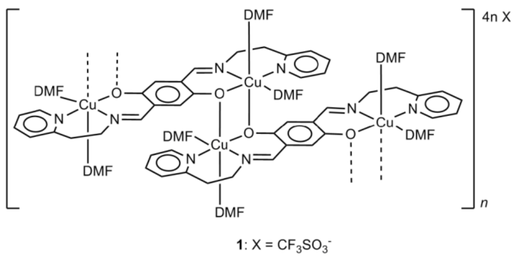


- NN1 shows similar crystal packing to non-functionalized tolaneNN-planar sheet structure
- NN2 and NN3 displays 3D hydrogen bonding network
- Possibility of transmitting magnetic-exchange interactions through hydrogen bond

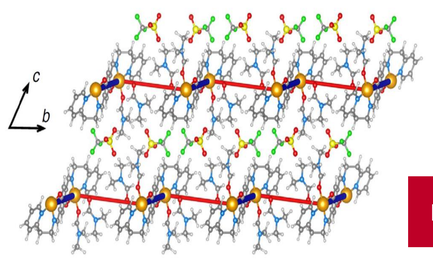
P. Ravat et al. *Crystal Growth& Design* **14**, 5840 (2014)

Achievements

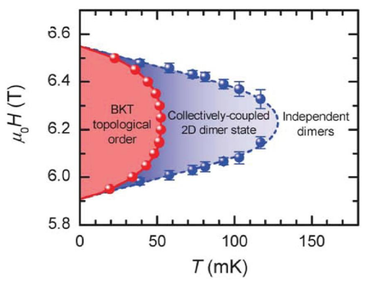
- **Cu(II)-*p*-hydroquinonate coordination polymer**



1: X = $CF_3SO_3^-$



B2 B3



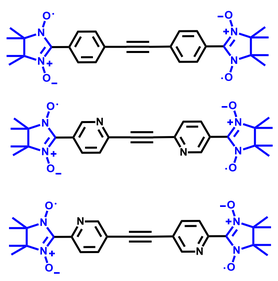
B1

completed: after 10 years 2D coupled spin- dimer system in a **Berezinskii-Kosterlitz-Thouless** Scenario

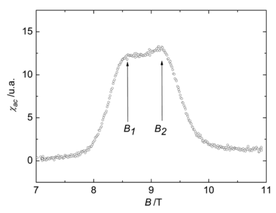
Strong interactions with B1, B2, and B3

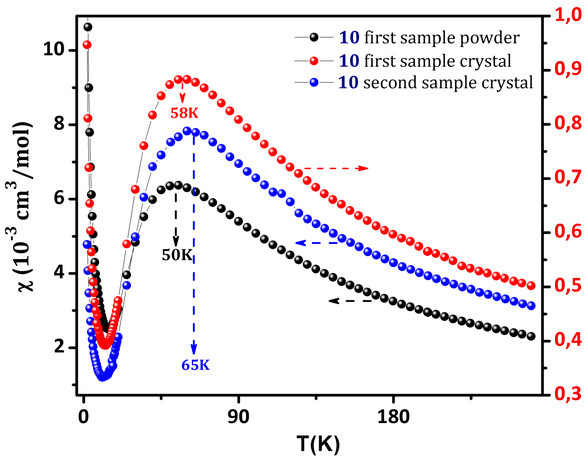
- Tutsch et al. , *Nature Commun.* **5**, 5169 (2014)

- **While a first working model was identified with a tolane biradical in the last period, further variations were considered:**



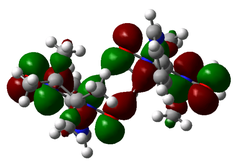
	Experimentally,	predicted DFT UBLYP, 6-31g(d)
	-9.6 K	8.6 K (X-ray)
	-10.7 K	9.8 K (X-ray)
	-91 K !!	-3.2 (X-ray) but why





- Strong Antiferromagn exchange interaction

- T_{max}= 58 K ~ $2J/k_B$= 91

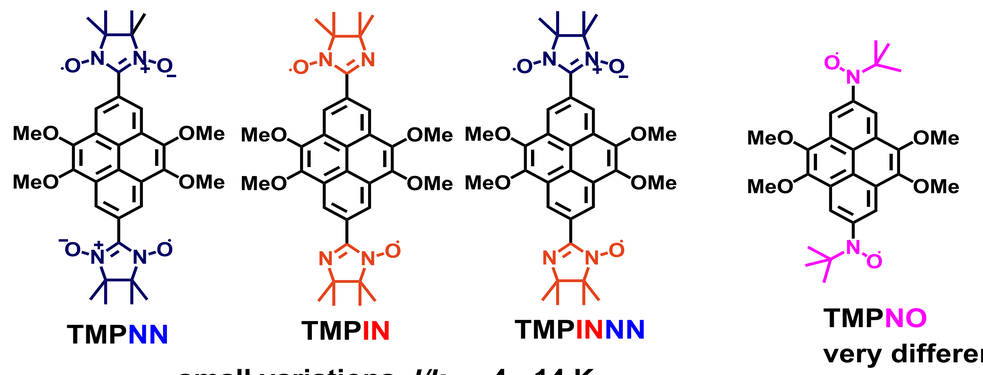


Short antiferromagnetic
Contact of 0.35 nm between 2 NO parts

Broken Symmetry DFT:
$\Delta E = E_{bs} - E_t$ = 60.7 cm^{-1} or 87.34 K

Borozdina et al. *J. Mater. Chem. C* **2,** 6618 (2014,) and manuscript in prep. 2015

Tetramethoxypyrenes (TMPs)

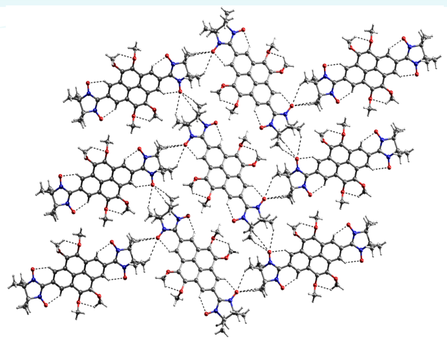


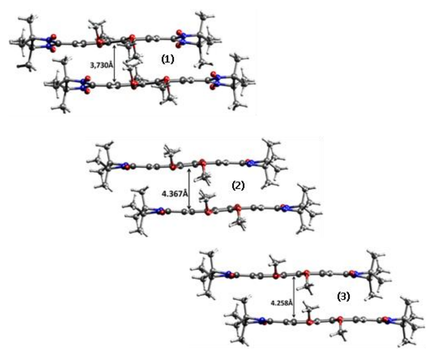
TMPNN **TMPIN** **TMPINNN** **TMPNO**

small variations J/k_B ~ 4 - 14 K

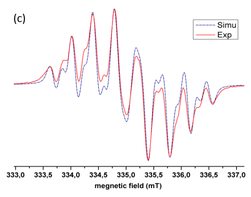
TMPNO very different J/k_B > 1000 K

All three biradicals possess similar unit cell parameters as well as crystal packing: Isomorphous. But different interlayer spacing





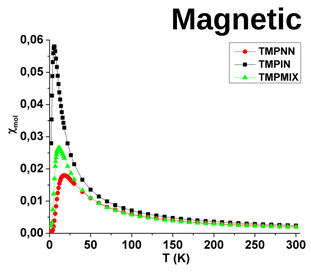
EPR spectrum of TMPINNN

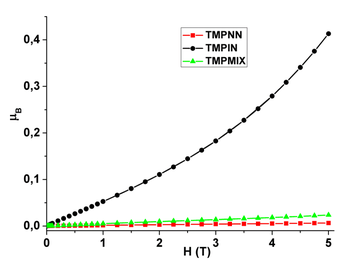


Magnetic properties of biradicals				
Radical	T_N [b] (K)	Θ [c](K)	J_{intra}(K) calc	J_{intra}(K) exp
TMPNN	18	-4.3	-14.5	-14.0
TMPIN	5.5	-5.7	-3.7	-4.5
TMPMIX	11.5	-4.2	-8.0	-9.0

[b]Néel temperature, [c]Weiss-temperature

Magnetic measurements





Ravat et al. *Org. Lett.* **15**, 4280 (2013), Ravat et al. *Chemistry, Eur. J.* **14**, 12041 (2014)

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